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ENVIRONMENTAL APPLICATIONS OF STEEL INDUSTRY SOLID WASTES

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Abstract

Various solid residues from steel industry were tested as adsorbents of hydrogen sulfide at high concentrations. Their performance towards the removal of thiocyanates from aqueous solutions was also studied. The H_2S adsorption capacity was evaluated at room temperature under both dry and wet conditions. The removal efficiency for thiocyanate ions from solution was evaluated at high ionic concentration. In both cases the results were compared to those of other adsorbents available in the literature. Despite the relatively low porous development, steel industry solid wastes show removal capacities for H_2S and SCN^- adsorption similar to those of conventional activated carbons with high surface area and pore volumes. The characterization of the physicochemical features of the materials has been used to track their adsorptive performance.

Keywords: slag, adsorption, hydrogen sulfide, thiocyanate

INTRODUCTION

Steel industries generate significant quantities of sludge and slag as wastes or byproducts every day. Although their composition depends on the generation source, they usually contain iron, carbon, calcium, or zinc (among others), which are interesting resources that can be recovered and reused [1].

On the other hand, most slag and sludges also contain relatively large amounts of toxic heavy metals that pose a serious problem if released to the environment. Along with the environmental challenges associated to their toxicity, the disposal of these residues represents a challenge from an economic viewpoint due to the costs linked to handling, management of hazardous wastes.

Despite that industries are continuously searching for solutions to reduce the amount of wastes being produced, for various industrial wastes an adequate way of recycling is not yet available. Within the current options of internal and external recycling, several valorisation routes are being considered, as well as landfilling and incineration. Disposal by landfill is inhibited by its rising cost, the implementation of The European Landfill Directive 99/31/EC [2] and the competing pressures for an ever diminishing supply of suitable landfill sites. At converse, incineration is expensive, it may give rise to potentially hazardous ash, and it is not always recommended for toxic industrial wastes. Thus, transforming industrial wastes into valuable materials or resources for further utilization is most desirable.

Their revalorization and re-using through the preparation of low cost adsorbents is considered a promising, environmentally friendly, energy efficient and cost-effective process [3].

This study investigates the revalorization of low cost solid residues generated by the steel industry. The aim is to evaluate the ability of the prepared materials for the removal of pollutants from gas (H_2S) and aqueous phase (thiocyanates).

EXPERIMENTAL

Sample preparation

Steelmaking slags as by-products of the steelmaking industry in Asturias (Spain) were used as the starting materials (samples SA and SV), and a particle fraction size between 212-500 m was selected. Details on the nomenclature assigned to the samples, and their main physicochemical characteristics are compiled in Table 1.

Table 1. Chemical composition (% wiegt) of the inorganic fraction (major elements) of the studied residues

Component	SA	SV
CaO	46.1	43.8
Fe_2O_3	18.2	21.1
SiO_2	14.1	16.5
MgO	4.5	5.5
MnO	4.2	4.1
Al_2O_3	2.5	2.5
P_2O_5	1.3	1.3
TiO_2	0.5	0.5
K_2O	0.1	0.1
Na_2O	0.03	0.02
LOI*	2.6	0.5

** loss on ignition*

Characterization

Porous texture of the samples was characterized by N_2 adsorption isotherms at 196 ºC. Before the experiments, the samples were outgassed under vacuum at 250 °C overnight. The isotherms were used to calculate the specific surface area, S_{BET}, and micropore volumes [4]. The samples were further characterized by elemental analysis using LECO automatic analyzers. Atomic absorption spectrometry was also used to determine the elemental composition of the inorganic components.

Adsorption of H_2S

Dynamic H_2S removal experiments were carried out in a fixed bed configuration, at room temperature. About 0.5 g of adsorbent were placed inside a quartz reactor (7 mm i.d.), ensuring uniform flow (150 ml min^{-1}) throughout the bed and avoiding axial dispersion. The H_2S initial concentration was settled in 700 and 1000 ppmv. Inlet and outlet H_2S concentrations were monitored using a μGC (Varian CP-4900) equipped with a thermal conductivity detector (TCD). The gas chromatograph was fitted with a 10 m PPQ column unit. Helium was employed as a carrier gas. The injector temperature was set at 110 °C; the oven temperature and inlet pressure were hold constant at 45 °C and 1.5 bar, respectively. All the experiments were carried out until bed exhaustion. Adsorption capacities x/M (mg H_2S /g adsorbent) were calculated by integration of the breakthrough curves as indicated elsewhere [5].

Adsorption from solution

The removal efficiency of the materials towards phenol and thiocyanates was explored from batch experiments at room temperature. About 1 g of the materials were accurately weighed and put in contact with a constant volume (i.e., 200 mL) of the pollutant solution, under stirring for 24 h. Afterwards, the adsorbate concentration in the supernatant liquid was measured, and the amount adsorbed -*q*- was calculated from the equation (1):

$$q = (C_0 - C_t)\, V/m \qquad (1)$$

where C_0 is the initial concentration, C_t the remaining concentration on the solution, V the volume of the solution and m the mass of the adsorbent.

RESULTS AND DISCUSSION

The objective of this study is to investigate the revalorization of solid wastes from the steelmaking industry as adsorbents. For this purpose, the retention capacities of these residues towards H_2S and SCN^- were determined and compared to those of other adsorbents reported in the literature [5-8].

The two selected slags SA and SV show rather similar chemical composition, which is characterized by a low content in organic matter (Table 1). As for the inorganic matter, the main detected elements are calcium, iron, silicon and magnesium, with small amounts of aluminum, manganese, or alkalines, among others. Traces of a few transition metals (copper, nickel) have also been detected. As for their surface features, the textural characterization by means of gas adsorption data (Table 2) and mercury porosimetry indicates that the slags are mainly macroporous materials, with low surface areas. Both presented a negligible volume of micropores and a small contribution of mesopores of large sizes (ca. 15-20 nm), as detected by gas adsorption data.

Table 2. Main textural parameters of the slags, evaluated by N_2 adsorption at -196 ºC.

	S_{BET} [$m^2\ g^{-1}$]	V_{TOTAL} [$cm^3 g^{-1}$]	$V_{MICROPORES}$ [$cm^3 g^{-1}$]	$V_{MESOPORES}$ [$cm^3 g^{-1}$]
SA	18	0.045	0.004	0.039
SV	20	0.044	0.006	0.037

Retention of H_2S

Figure 1 shows the breakthrough curves for H_2S on the as-received studied samples. The dynamic tests were also carried out in pre-humidified materials (wet series), so as to evaluate the effect of moisture in the retention ability of hydrogen sulfide.

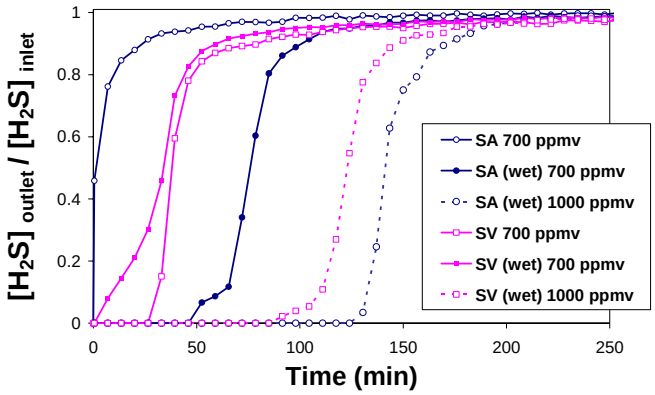

Figure 1. Breakthrough curves for H_2S adsorption at high concentrations on the as-received and pre-humidified (wet) samples.

The corresponding adsorption capacities obtained from integration of the breakthrough curves at the saturation point are collected in Table 3. Important differences are observed in the retention times and the shapes of the curves, indicating variation in the kinetics and capacity for H_2S adsorption of these materials. The effect of pre-humidification of the slag beds is very strong, and does not follow the same trend in the two tested materials. The H_2S retention in the as-received SA slag (dried) was greatly improved after humidification. At converse, this effect was not observed in SV which H_2S retention decreased slightly after humidification. Furthermore, wet SA sample outperforms the adsorptive behavior of both dried and wet SV. These differences are less evident as the gas initial concentration increases from 700 to 1000 ppmv. Notwithstanding the uptake increases with the gas initial concentration (Table 3 and Figure 1).

The beneficial impact of even small quantities of water on the adsorbent in the retention of H_2S has already been reported in highly porous carbon-based materials [9]. Such performance has been linked to the basic character of the adsorbents, and to reactive mechanisms of H_2S adsorption, involving oxidation. Given the chemical features of the slag, it is reasonable to expect a similar behavior. Wetting of the slag may provoke important changes in their chemical composition. Major hydration rations occur in the presence of calcium and magnesium oxides, and calcium silicates, according to [10]:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (3)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO + 2SiO_2 + 3H_2O + Ca(OH)_2 \quad (4)$$

Then, the basicity of the slags originated upon hydration of calcium and magnesium species might be considered as responsible of the relatively high adsorption performance of these materials for H_2S.

An important fact that should be highlighted is the relatively high retention capacity of these residues despite their low porous features. Such behavior is particularly attractive from a technological point of view, since it allows the direct revalorization of the residue without any additional processing. Moreover, they present similar or higher H_2S adsorption capacities when compared to other adsorbents -both commercially available and waste-derived- reported in the literature that possess much larger surface areas and pore volumes [5-7].

Table 3. Adsorption capacities of the studied slags towards H_2S and SCN^-. For comparison, the performance of conventional adsorbents has also been included.

	x/M dry [mg/g][a]	x/M wet [mg/g][b]	x/M wet [mg/g][b]	SCN^- [µmol/g][c]
SA	7.5	29.8	62.6	25.9
SV	24.8	15.6	67.6	17.2
	Remarks		SCN^-[µmol/g][c]	
Q	Activated carbon		82.4	
Z13X	Zeolite		22.1	
FN6	Diatomite		9.3	

a Initial concentration 700 ppmv H_2S
b Initial concentration 1000 ppmv H_2S
c Initial concentration 300 ppm SCN^-

Removal of SCN^-

Thiocyanates retention of the slags is shown in Table 3, along with the values of conventional adsorbents of different nature. The uptake of SCN^- in the slags is rather low, likely due to their poor pore structure. The retention is lower than that of activated carbon, but the values are similar of higher than those of inorganic materials as zeolites and diatomites. Although some differences are observed in the performance of the two studied slags, these results suggest that specific interactions are formed between the inorganic matrix and SCN^-. Thus, it seems that as-received slags without further processing may be used for the removal of SCN^- from aqueous phase. Further studies are ongoing to

create an adequate pore network that may enhance the uptake.

CONCLUSIONS

As-received slags from steelmaking industry have shown large adsorption capacities towards H_2S after pre-humidification of the adsorbent bed. This demonstrates that they may be used without the need of any additional processing. Despite the lack of a well developed porous network, the removal efficiency towards SCN^- is similar to that of other commercial inorganic adsorbents, which points out the adequate chemical composition of the slags for the retention of thiocyanates.

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